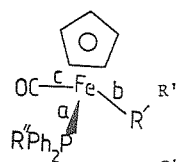


09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS



R''	Ph	NEt ₂	Ph
a	2.193(1)	2.190(1)	2.205(1) ^o
b	1.964(3)	1.972(3)	1.974(5)
c	1.733(3)	1.732(3)	1.729(5)
ab	89.3(1)	89.0(1)	92.0(2) ^o
ac	92.1(1)	94.3(1)	91.7(2)
bc	94.8(1)	95.4(1)	93.7(2)

Since the inter-bond angles at the iron atom are close to 90° the coordination at iron is better described as octahedral not tetrahedral. The relative configuration of the new chiral centre in Ia and Ib, and the prochiral centre in Ic is established. The carbon monoxide ligand is in each compound *anti* to the carbon oxygen bond. If this *anti* conformation is preferred in the enolate (R' = -OC=CHR) the approach of an electrophile will occur on the face of the enolate which is not shielded by a phenyl group of the phosphine ligand thus determining the stereochemistry of the product.

References

- G. J. Baird, J. A. Bandy, S. G. Davies and C. K. Prout, *J. Chem. Soc., Chem. Commun.*, 1983, 1202.

09.4-1 CRYSTAL AND MOLECULAR STRUCTURE OF DICYANO-COBYRINIC ACID HEPTAMETHYL ESTER.

by J.C.A. Boeyens, A.J. Markwell and M.S. Shaikjee
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The crystal and molecular structure of the vitamin B₁₂ derivative, dicyano-cobyrinic acid heptamethyl ester, has been determined. The structure was solved (4270 independent reflections measured on a diffractometer) using standard Fourier methods, with initial phasing using the cobalt atom, to an R-factor of 0.1068. The space group is P1 with Z = 2; unit cell dimensions, a = 16.332, b = 13.252, c = 14.475 Å; α = 90.0, β = 109.75, and γ = 90.0°. The two cyanide ligands are bonded in a linear fashion to the cobalt, the one in the 'lower' position being H-bonded to an isopropanol molecule. There are no significant differences between the two crystallographically independent molecules, except for their orientations in the unit cell.

09.4-2 DEVELOPMENT OF KNOWLEDGE OF THE LIGAND TRANS-STRENGTHENING. By L.A. Aslanov, Chemistry Department, Moscow State University, Moscow, USSR.

In development of the earlier investigation (O.A. Reutov et al., *Koordinatsionnaya Khimiya* (1982) 8, 1161 (Russ.)) the ligand trans-strengthening in octahedral complexes of tin (IV) was studied by the X-ray crystallography methods. This type of interaction is apparent in iodine complexes, e.g. EtSnI₃. 2HMPTA (i) (HMPTA=hexamethylphosphotriamid). It can be described as a shortening of the Sn-I_{trans} interatomic distance 2,634(2) Å in trans-position to Et-group. This distance is shorter than Sn-I in SnI₄.Dipy (ii), SnI₄.2TPPO (iii) (Dipy=2,2'-dipyridyl, TPPO=triphenylphosphin-oxide) 2,782(2)-2,819(2) Å, and even shorter than Sn-I in SnI₄ 2,69(2) Å (F.Meller, I.Fan-kuchen, *Acta Cryst.* (1955) 8, 343). Such anomalous shortening of Sn-I_{trans} inspite of the increase of coordination number from 4 to 6 is found first. It can be explained by the electron-donating Et-ligand influence and is observed simultaneously with displacement of the equatorial ligands from equatorial plane to I_{trans}. Cis-weakening of Sn-I_{cis} bonds in (i) in comparison with Sn-I in (ii) and (iii) is relatively smaller (3,8%) than trans-strengthening (5,8%). These facts show that trans-strengthening is a special phenomenon, which determines together with cis-weakening the structures of octahedral tin(IV) complexes. The single crystals without statistical distribution of alkyl groups and halogen atoms (L.A. Aslanov et al., *Organometal. Chem.* (1978) 144, 39) were grown for compounds Alk_nSnHal_{4-n}. 2L (Alk=Et, Bu; n=0,1; Hal=Cl, Br; L=TPPO, HMPTA etc.). The Sn-Cl bond distances give no information about trans-strengthening, but the trans-strengthening was found by IR- and Raman - spectroscopy both in chlorine and bromine complexes. The shortening of Sn-Br_{trans} distances in bromine complexes is smaller in comparison with Sn-I_{trans} bonds in iodine complexes. The Alk Sn Hal₃. 2L (L=N-donor ligands) compounds have a structural peculiarity: nitrogen atom is situated in trans-position to Alk-group without shortening of the Sn-N bond; cis-weakening with Hal=I becomes moderate. The (Alk Sn Cl₅)²⁻ anion complexes have the shortest Sn-Cl bond in trans-position to Alk-group, but this bond is not shorter than one in (Sn Cl₆)²⁻. Investigation of the (Alk Sn Hal₅)²⁻ (Hal=Br, I) complexes is in progress.